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Fractionation and health risks of atmospheric particle-bound As and heavy metals in summer and winter

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HIGHLIGHTS

- Seasonal variation of elemental contents, distribution and sources in TSP and $PM_{2.5}$
- Impact of season on distribution and sources of elements is higher than particle size.
- Bioavailable fractions of Zn, Pb, As and Cu in atmospheric particles were above 60%.
- Accumulative health risks to residents via inhalation and ingestion exposure to $PM_{2.5}$
- Children suffer more potential carcinogenic and non-carcinogenic risks than adults.

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ABSTRACT

Elemental chemical speciation in atmospheric particles determining their bioavailability and toxicity is an implication for human health assessment. Total suspended particulates (TSP) and fine particulate matter ($PM_{2.5}$) in summer and winter (Nanjing, China) were therefore collected for assessing the fractionation and human health risks associated with As and heavy metals (Cu, Pb, Zn, Ni, Co, Cr, Cd and Mn). Elements' contents and their enrichment factors in TSP and $PM_{2.5}$ varied greatly with the season. Principal component analysis and cluster analysis confirmed the seasonal variation of these elements. Based on the optimized Community Bureau of Reference (BCR) sequential extraction procedure, the elemental distribution in TSP and $PM_{2.5}$ differs dramatically. Labile and bioavailable fractions of Zn, Pb, As and Cu in atmospheric particles were more than 60%. Based on the bioavailable fractions, the carcinogenic risks are mainly from the ingestion of Pb in $PM_{2.5}$. For non-carcinogenic risk, accumulative multi-elements via inhalation and/or ingestion exposure can impact both children and adults, while single element ingestion such as As, Pb and Co may pose risks to children. More attention should be paid to alleviate non-carcinogenic health risks posed by particle bound toxic elements via ingestion and inhalation exposure.

1. Introduction

Atmospheric particle is one of the serious ambient air pollutants throughout the world and has been classified as group 1 contaminants by the International Agency for Research on Cancer (IARC). Recent studies show that atmospheric particles are enriched with metallic elements (Okuda et al., 2008; Wu et al., 2007). Without biodegradation, heavy metals from atmospheric particles may accumulate in human being via inhalation and ingestion, which may be linked with both short-term and long-term adverse health effects, especially for children (Kampa and Castanas, 2008; Wild et al., 2009).

It is well known that the toxicity and mobility of heavy metals in the environmental medium are controlled by their chemical speciation. X-ray absorption spectroscopy (XAS) is an effective tool to identify chemical species of heavy metals in environmental samples (Barrett et al., 2010; Da Silva-Cadoux et al., 2012) including atmospheric particles (Osan et al., 2010). However, the scarcity of XAS limits its application in the atmospheric research, and the operationally defined metal fractions provide considerable insights into the environmental behavior of heavy metals (Filgueiras et al., 2002). The optimized BCR sequential extraction procedure (proposed by the Community Bureau of Reference (BCR)) is one of the widely used protocols and divides heavy metals into four operationally defined chemical fractions: acid extractable, reducible, oxidizable and residual fractions (Larner et al., 2006; Sahuquillo et al., 1999). Although it has been used in the investigation of the atmospheric particle-bound heavy metals (Astolfi et al., 2006; Canepari et al.,

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2010; Feng et al., 2009), health risks related to the fractions of these heavy metals are still unclear.

The Yangtze River Delta (YRD) region, the lower reaches of the Yangtze River, is one of the three fastest growing economic development regions in China, which also have severe haze-pollutions (Kang et al., 2013; Zhang et al., 2012). Haze pollution over the YRD is increasing during the past decade (Che et al., 2009). As one of the three main center cities in the YRD, Nanjing (118°22′ and 119°14′E, 31°14′ and 32°37′N) is also the capital city of Jiangsu Province. The occurrence of hazy days in Nanjing kept increasing from 1961 to 2005 and the annual hazy days in Nanjing were about 130 d during 2001 to 2006 (Tong et al., 2007). However, it was 211 d in 2009 (Song et al., 2012) and 212 d in 2010 (Wang et al., 2012), respectively. Atmospheric particles as the key components of the hazy episode can be one of the most important environmental issues in Nanjing. Toxic elements bounded with these particles may pose potential health risks to local residents (Hu et al., 2012). In the present study, atmospheric particles (TSP and $PM_{2.5}$) were collected during the summer and the winter from two sampling sites in Nanjing. The main objectives of this study were to investigate the fractionation of particle bound metals in different sampling seasons and to assess the human health risks posed by As and heavy metals via inhalation and ingestion exposure. The combination of chemical fractionation and health risk assessment can offer valuable information to the policymaker than the analysis of metallic total contents in atmospheric particles.

2. Materials and methods

2.1. Sampling

Atmospheric particles (TSP and $PM_{2.5}$) were collected in the summer (from June to August) and the winter (from November to January) during 2010 and 2011 from two previous sampling sites in Nanjing; one in the traditional center district (Gulou, the campus of Nanjing University) and the other in the suburbs (Pukou, the campus of Nanjing University of Information Science & Technology) (Hu et al., 2013). Briefly, four TSP samples and three $PM_{2.5}$ samples were collected monthly on polytetrafluoroethylene (PTFE) filter membranes (20×25 cm^2) using a large-volume air sampler (HY-1000, Qingdao Henyuan Instruments Co. Ltd., Qingdao, China) with a flow rate of 1.05 m^3/min. The sampling duration was set at 8 h for TSP samples and 16 h for $PM_{2.5}$ samples. Overall, 48 TSP samples and 36 $PM_{2.5}$ samples were obtained in the present study. All filter membranes were equilibrated in a desiccator for 48 h and then weighed before and after aerosol sampling to determine the aerosol mass. The filter membranes were then placed into a glass vial with a Teflon-lined cap and stored at −20 °C for analysis. The field blank filter membranes were set at the same time.

2.2. Analysis of elemental contents

The elemental contents in TSP and $PM_{2.5}$ were analyzed using digestion method (US EPA 3051b) with the same operation detail as our previous study (Hu et al., 2013). Digested solutions after microwave pretreatment were evaporated to near dryness, then dissolved in 65% HNO_3, and brought to volume with Milli-Q water. Solutions were stored in 25 ml high-density polyethylene vials at 4 °C prior to instrumental analysis. The standard reference material (GBW07405 bought from the National Research Center for Geoanalysis, China) was used to verify the precision and accuracy. The element recovery percentage from the standard reference material was between 90.1% and 106.4%. Elemental concentrations (As, Cr, Cu, Mn, Pb, Zn, Ni, Co and Cd) in the digestion solutions were measured by using inductively coupled plasma optical emission spectrometry (ICP-OES Optima 5300, Perkin-Elmer SCIEX, USA) and inductively coupled plasma mass spectrometry (ICP-MS Elan 9000, Perkin-Elmer SCIEX, USA). During ICP-MS analysis, ^{115}In was used as the internal standard at 20 μg/l in 2% HNO_3.

2.3. Optimized BCR sequential procedure for extraction of toxic metals

Four operationally defined metal fractions isolated using the optimized BCR sequential extraction procedure were: 1) acid soluble fraction (F1): metals are soluble and exchangeable fraction and bound to carbonates (0.11 mol l^{-1} CH_3COOH, for 16 h); 2) reducible fraction (F2), metals bound to Fe/Mn oxides (0.5 mol l^{-1} $NH_2OH{\cdot}HCl$, pH 1.5, for 16 h); 3) oxidizable fraction (F3), metals bound to organic matter and sulfides (30% H_2O_2 acidified with HNO_3 to pH 2 at 85 °C for 2 h, then followed by the extraction with 1 mol l^{-1} CH_3COONH_4, pH 2–3, for 16 h) and 4) residual fraction (R, digestion with aqua regia) (Larner et al., 2006; Sahuquillo et al., 1999). During successive extraction steps, separation was performed by centrifugation at 3500 rpm for 20 min. The supernatant was decanted into polyethylene containers and stored in a refrigerator at 4 °C prior to ICP-OES and ICP-MS analyses. The recovery of the sum of the four fractions (F1, F2, F3 and R) to the total concentrations of the trace metals during the sequential extraction procedure was performed as an internal check of extraction process.

2.4. Statistical analyses

Statistical analyses of the elemental data were carried out using SPSS 16 for Windows (SPSS Inc., Chicago, IL, USA). An independent sample t-test was used to determine the difference in elements' concentrations in TSP and $PM_{2.5}$ between summer and winter. The $p < 0.05$ was taken to indicate statistical significance. Principal component analysis (PCA) and R-mode cluster analysis (CA) were used for source apportionment studies without source profiles (Viana et al., 2008). One-sample Kolmogorov–Smirnov test was used to test the normal distribution for the variables investigated after logarithmic transformation (Webster and Oliver, 2001) suggesting that variables were normally distributed at $p < 0.01$. Varimax with Kaiser Normalization Rotation was applied to maximize the variances of the factor loadings.

3. Results and discussion

3.1. Elemental contents in atmospheric particles

The descriptive statistics of elemental contents (As, Cd, Cr, Cu, Mn, Ni, Pb, Co and Zn) in TSP and $PM_{2.5}$ were listed in Table 1. The coefficients of variation (CV) for metal contents (Table 1) indicated the variation of metal contents within the same season, which may be caused by meteorological factors such as wind speed and direction. The contents of Cu, Pb, Mn and Zn were generally higher than those of the other elements in TSP and $PM_{2.5}$. In general, the studied elemental contents in both TSP and $PM_{2.5}$ were higher in winter than in summer. For example, there were significant differences between summer and winter in the contents of As, Cu, Mn, Ni, Pb, Co and Zn in TSP and As, Cr, Cu, Mn, Pb and Co in $PM_{2.5}$ ($p < 0.05$). In winter, the increased elemental concentrations of atmospheric particulates may contribute to the long-range transport of air contaminants from Northern China. In Northern China from November to next March, large volume of particulates were released from coal burning for urban central heating system then transported to the south by the northeastern wind. The particle-bound elemental contents and seasonal variation in the present study were consistent with the previous investigations of Beijing, Shenyang, Lanzhou, Chongqing, Shanghai, Wuhan, and Guangzhou (Hu et al., 2010). For example, the average concentrations of metallic elements in $PM_{2.5}$ during 1995–2005 were in the order of Zn > Pb > Cu > Mn > Cr > Cd for Asian countries (Wu et al., 2007). In the present study, the average Cu contents in $PM_{2.5}$ were higher than those in Shanghai, while As and Cd were not (Chen et al., 2008). The contents of the elements in TSP tested were similar to or slightly lower than those in Beijing, from March 2001 to March 2006 (Okuda et al., 2008). For TSP and $PM_{2.5}$ Pb, Cu, Zn, Cr, and Ni